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Evaluation of dilute hydrochloric acid and acid ammonium oxalate as extractants for some heavy metals from Nile River sediments

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The suitability of a 0.5 M HCl solution for extraction of Fe, Mn, Cd, Co, Cu, Pb, and Zn from Nile River sediments was evaluated by comparing its effectiveness with that of conventional acid ammonium oxalate (Tamm's solution) and aqua regia extraction solutions. The present study has shown that although the extraction data indicate that both 0.5 M HCl and acid ammonium oxalate solutions are able to extract heavy metals simultaneously from the adsorbed, organic, and precipitated phases of Nile sediments, the 0.5 M HCl solution is preferred. It provides a rapid, reliable, and inexpensive method of measuring environmentally mobile metal concentrations in the aquatic sediments. From an analytical chemistry point of view, the 0.5 M HCl extracts do not clog the atomizer of the spectrophotometer. Extraction with dilute HCl solution obviates the need to use chemicals, some of which are toxic or not available readily as a high-purity grade. A standard extraction method should be relatively simple, to conduct a routine analysis of large numbers of sediment samples, yet at the same time it should provide sufficient information for assessment of the environmental impact of particulate metals. Therefore, extraction with 0.5 M HCl solution is very suitable for heavy-metal pollution monitoring in the Nile River

Keywords: Sediment; Extraction; Pollution; River Nile; Heavy metals

1. Introduction

Chemical pollutants into a river, whether through natural (erosion of its drainage basin) or artificial (anthropogenic) means, can be introduced in dissolved or particulate form. Depending on the physicochemical conditions, pollutants in dissolved form can precipitate later as hydroxides, carbonates, or other sediment components. They can also be adsorbed by the iron or manganese oxides and hydroxides or coprecipitate with these, or form dissolved organic or inorganic complexes [1–3]. In particulate form, associated with suspended matter, the pollutant can, under favourable hydrological conditions, be deposited on the river bottom.

Analysis of river sediments is a good indicator of the river water quality [4]. They are less variable than the overlying water column. Furthermore, the analysis of sediments eliminates

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the problem of erratic fluctuations which are often observed in water, and the contents are generally well above detection limits, which is not always the case in water [5–7]. Today, metallic pollutants have a great ecological significance due to their toxicity and cumulative behaviour [8]. They are not biodegradable, in comparison with most pollutants, and undergo a global eco-biological cycle [9] in which natural waters are the main pathway. Knowledge of the metallic pollutant concentrations in sediments and of their evolution is of interest because while they act as traps, catching pollutants, they can also be considered to be reservoirs capable of releasing some of their constituents under certain physico-chemical conditions (variation in pH, redox potential, complexation, early diagenesis, etc.).

The total element concentration provides important knowledge about the pollution level, if the background or geochemical composition is known. However, the natural or anthropogenic origin of elements is rather difficult to determine. In water systems, the speciation of an element determines the biological availability and chemical reactivity (sorption/desorption, precipitation/dissolution) towards other components of a system. Many different partial extraction methods have been proposed; nitric, hydrochloric, and acetic acids have all been used at a variety of concentrations, reaction times, and temperatures [10–13]. Hydrochloric acid is a strong acid that will attack key labile phases in the sediment matrix [14]. Its reducing properties help liberate metals from Fe and Mn oxides [15], which can be a major sink for trace metals in oxic sediments [16–18]. It is also efficient at decomposing labile organic phases [19, 20] and amorphous sulphides that control metal bioavailability in anoxic and partially oxidized sediments [15, 21]. However, a number of different extraction times and acid concentrations have been proposed, varying between 0.5 and 24 h and 0.05 and 3.0 M [12, 17, 21].

Extraction with acid oxalate (Tamm's solution, pH 3.3) [22] is conventionally used to shed light on the phase distribution of heavy metals in soil and aquatic sediments. Use of the atomic absorption spectrophotometer may sometimes be hampered by the tendency of the nebulizer and burner slot to clog when solutions of high salt concentration are aspirated. Acid oxalate is often especially troublesome in this respect [23]. Also, the chemicals used in the preparation of this extractant are toxic and/or not available readily in a high purity grade. Therefore, the main purpose of this study was to evaluate the suitability of 0.5 M HCl solution for extraction of metals associated with the major components of the Nile sediments by comparing its effectiveness with that of acid oxalate and aqua-regia extraction techniques.

2. Material and methods

2.1 Sampling

Eleven sediment samples were collected using a Peterson grab sampler from the main stream along the Nile River from Aswan to Giza (figure 1). The samples were air-dried and dried in an electrical furnace at 105°C for 24 h, then gently broken and thoroughly mixed. Representative sub-samples were prepared and kept in polyethylene bags.

2.2 Separation of the <63 µm sediment fraction

Physical dispersion of the sediment samples was performed by shaking 150 g of sediment overnight with 150 ml of distilled water. The <63 µm sediment fraction was split from the gross sediment sample suspension using wet sieving [24]. The separated sediment fraction

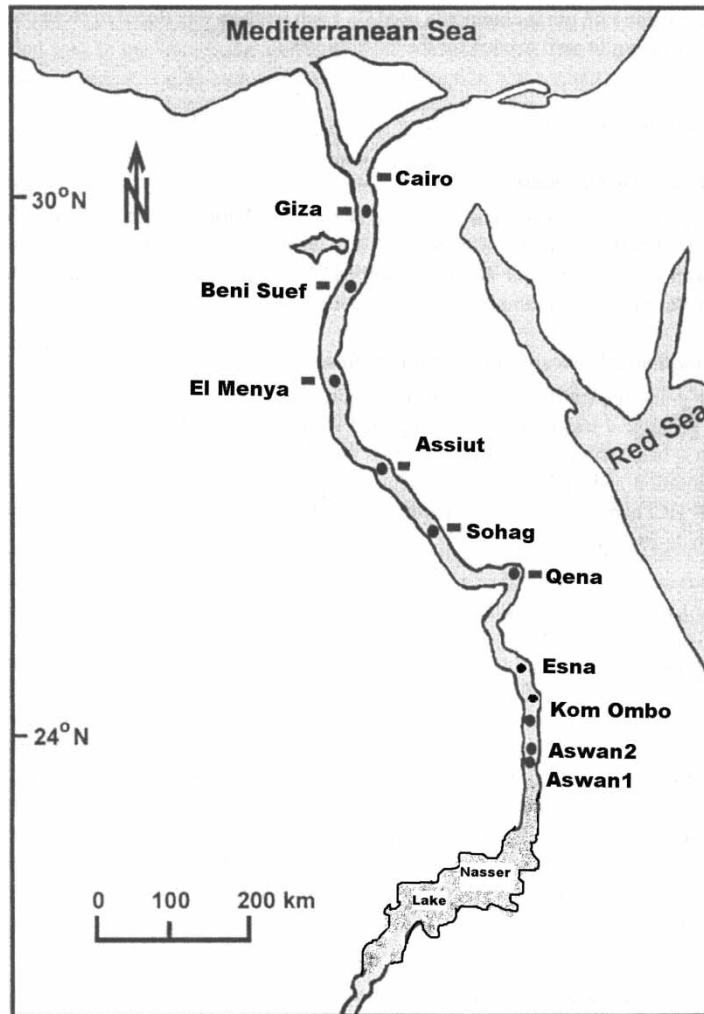


Figure 1. Map of the sampling location along River Nile from Aswan to Giza.

was then oven dried at 150 °C, and an appropriate amount was ground in an agate mortar and used for chemical extraction and chemical analysis of sediment components.

2.3 Extraction procedures and preparation of solutions

All reagents used in this study were of analytical grade (A.R.). The water used was doubly distilled in Pyrex apparatus, and redistillation was carried out using alkaline permanganate solution. All glassware and plastic bottles used in this study were previously soaked in 14% HNO_3 (v/v) and rinsed with double-distilled water. The ground $<63 \mu\text{m}$ sediment fraction was used in all selective extraction procedures and chemical analysis of sediment components.

2.3.1 Extraction with 0.5 M HCl solution. One-gram portions of each sediment samples were treated individually with 0.5 M HCl solution at sediment:extraction ratios of 1:10, 1:20,

1:25, and 1:50. The sediment–HCl suspensions were shaken for 1, 2, 3, and 5 h on a wrist-action shaker at room temperature, the suspensions were then filtered through Whatman No. 42 filter papers, and the filtrates were kept in polyethylene bottles for chemical analysis.

2.3.2 Extraction with acid oxalate, pH 3.3 (Tamm's solution). Fifty millilitres of acid oxalate solution (0.1 M oxalic acid, 0.175 M ammonium oxalate) [23] was added to 1 g of dried sediment sample (63 μm) in a 125 ml polyethylene bottle and shaken at room temperature using a wrist-action shaker for 5 h. The suspension was filtered through Whatman No. 42 filter paper, and then the filtrate was collected in a 125 ml polyethylene bottle to measure the element concentrations in the extracts.

2.3.3 Extraction with aqua regia (3:1 v/v, HCl:HNO₃). One gram of dried sediment sample (<63 μm) was digested with a mixture of 9 ml of HCl (12 M) and 3 ml of HNO₃ (14.9 M) for 2–3 h at 60 °C. The mixture was heated on a water bath at 105 °C for 1 h, and then the temperature was increased to 140 °C until near dryness. After cooling, 12.5 ml of 2.5 M HCl was added, and the mixture was rewarmed at 80 °C for 20 min. The solution was filtered through Whatman no. 42 filter paper and made up to 50 ml with double-distilled water.

2.4 Determination of organic carbon and carbonates

Organic carbon in sediment samples was determined by the Walkley–Black method [25]. For carbonates, 2 g of dried sediment sample was weighed into a 250 ml conical flask, 40 ml of 0.5 N HCl was added, and the mixture was swirled for mixing. The contents were then left to stand for 1 h. The excess acid was titrated with a standard solution of 0.5 N NaOH using phenolphthalein as an indicator. The percentage of carbonate was calculated.

2.5 Physico-chemical measurements

The pHs of the sediment samples were measured by a pH meter (Orion Research Model SA11/Digital pH meter). Electrical conductivity was measured using a conductivity meter (YSI Model 33 S.C.T. Meter VSA).

2.6 Elemental analysis

The concentrations of treated elements were determined by atomic absorption for Fe, Mn, Ca, Mg, Cd, Co, Cu, Pb, and Zn and by atomic emission for K⁺ and Na⁺. A flame atomic absorption spectrophotometer (Model 3110 Perkin-Elmer) equipped with a digital and direct concentration readout and an air–acetylene burner was used. Single-element hollow cathode lamps and standard instrumental conditions were used for each element. Suitable precautions were taken to minimize interferences when necessary. Element concentrations in the different leachates were quantified by appropriate calibration curves of standard element concentrations prepared in the extraction solutions.

3. Results and discussion

The results of extraction by aqua regia, acid ammonium oxalate, and HCl are presented in tables 1–6, and are represented graphically in figures 2–7. These are expressed as $\mu\text{g g}^{-1}$, in

Table 1. Total (aqua-regia-digestible) and extractable Fe and Mn concentrations ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

| Location | Fe | | | Mn | | |
|-----------|--------|-----------------|--------------------------|-------|-----------------|--------------------------|
| | Total | HCl-extractable | Acid-oxalate-extractable | Total | HCl-extractable | Acid-oxalate-extractable |
| Aswan 1 | 19 030 | 8670 | 5041 | 650 | 410 | 325 |
| Aswan 2 | 23 530 | | 6698 | 550 | 460 | 275 |
| Kom-Ombo | 18 985 | 6850 | 3853 | 3500 | 870 | 570 |
| Edfu | 18 610 | 11 065 | 4851 | 2150 | 800 | 250 |
| Esna | 22 660 | 9525 | 5760 | 1850 | 813 | 400 |
| Qena | 22 660 | 10 145 | 3072 | 5800 | 1255 | 425 |
| Sohag | 18 420 | 10 753 | 2940 | 3050 | 983 | 775 |
| Assiut | 20 275 | 9385 | 9887 | 5250 | 793 | 375 |
| El Menya | 20 660 | 6770 | 5867 | 1750 | 590 | 275 |
| Beni Suef | 21 650 | 8290 | 2853 | 750 | 736 | 375 |
| Giza | 18 275 | 6950 | 6615 | 1850 | 725 | 575 |
| Mean | 20 432 | 8826 | 5222 | 2468 | 767 | 420 |

Table 2. Total (aqua-regia-digestible) and extractable Ca and Mg concentrations ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

| Location | Ca | | | Mg | | |
|-----------|--------|-----------------|--------------------------|--------|-----------------|--------------------------|
| | Total | HCl-extractable | Acid-oxalate-extractable | Total | HCl-extractable | Acid-oxalate-extractable |
| Aswan 1 | 14 670 | 14 477 | * | 6450 | 4995 | 1807 |
| Aswan 2 | 14 470 | 13 410 | * | 7665 | 7720 | 2928 |
| Kom-Ombo | 15 780 | 9422 | * | 8220 | 7260 | 2113 |
| Edfu | 17 940 | 15 543 | * | 8093 | 6210 | 3877 |
| Esna | 15 543 | 10 200 | * | 7905 | 6022 | 3252 |
| Qena | 17 313 | 11 880 | * | 7298 | 6530 | 2085 |
| Sohag | 19 311 | 15 360 | * | 5925 | 6765 | 2491 |
| Assiut | 17 334 | 10 440 | * | 6758 | 6499 | 2422 |
| El Menya | 16 485 | 15 240 | * | 6150 | 6431 | 2191 |
| Beni Suef | 14 780 | 11 400 | * | 11 407 | 9270 | 3516 |
| Giza | 18 490 | 14 790 | * | 7245 | 5690 | 2844 |
| Mean | 12 586 | 18 682 | * | 7556 | 6672 | 2684 |

Table 3. Total (aqua-regia-digestible) and extractable K and Na concentrations ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

| Location | K | | | Na | | |
|-----------|-------|-----------------|--------------------------|-------|-----------------|--------------------------|
| | Total | HCl-extractable | Acid-oxalate-extractable | Total | HCl-extractable | Acid-oxalate-extractable |
| Aswan 1 | 910 | 990 | 238 | 6400 | 3158 | 2863 |
| Aswan 2 | 820 | 880 | 205 | 3580 | 2605 | 1647 |
| Kom-Ombo | 1150 | 763 | 245 | 6010 | 3742 | 1910 |
| Edfu | 1265 | 898 | 455 | 5090 | 2886 | 4033 |
| Esna | 1625 | 958 | 198 | 5315 | 2916 | 971 |
| Qena | 1120 | 893 | 833 | 5600 | 3090 | 1107 |
| Sohag | 1070 | 997 | 178 | 3735 | 2653 | 589 |
| Assiut | 1080 | 855 | 218 | 5885 | 3521 | 450 |
| El Menya | 1005 | 990 | 185 | 4840 | 3670 | 1283 |
| Beni Suef | 1585 | 993 | 178 | 7210 | 2935 | 3905 |
| Giza | 1135 | 695 | 145 | 4970 | 2953 | 614 |
| Mean | 1161 | 901 | 280 | 5330 | 3103 | 1761 |

Table 4. Total (aqua-regia-digestible) and extractable Cd and Co concentrations ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

| Location | Cd | | | Co | | |
|-----------|-------|-----------------|--------------------------|-------|-----------------|--------------------------|
| | Total | HCl-extractable | Acid-oxalate-extractable | Total | HCl-extractable | Acid-oxalate-extractable |
| Aswan 1 | 2.0 | 1.9 | * | 25.6 | 13.3 | 4.0 |
| Aswan 2 | 3.0 | 3.0 | * | 25.0 | 13.3 | 3.0 |
| Kom-Ombo | 4.0 | 3.0 | * | 32.0 | 12.8 | 3.0 |
| Edfu | 3.0 | 2.0 | * | 26.0 | 16.8 | 3.0 |
| Esna | 3.0 | 3.0 | * | 25.0 | 13.0 | 2.2 |
| Qena | 3.5 | 4.0 | * | 34.0 | 14.5 | 2.0 |
| Sohag | 3.5 | 2.9 | * | 33.0 | 17.5 | 2.0 |
| Assiut | 3.5 | 3.0 | * | 31.0 | 12.5 | 4.0 |
| El Menya | 3.5 | 3.0 | * | 30.6 | 12.5 | 4.0 |
| Beni Suef | 3.5 | 3.5 | * | 36.0 | 16.5 | 5.0 |
| Giza | 3.5 | 2.8 | * | 27.0 | 22.8 | 5.0 |
| Mean | 3.3 | 3.0 | * | 30.0 | 15.0 | 3.4 |

*Below the detection limit.

the $<63 \mu\text{m}$ dry sediment fraction. The behaviour of the heavy trace elements (Cd, Co, Cu, Pb, and Zn) is of primary interest, but these cannot be considered in isolation. Results for such relevant major elements as Fe, Mn, Ca, Mg, K, and Na and other sediment characteristics (CaCO_3 , organic carbon, and grain-size distribution) (table 7) are given to provide a basis for comparison.

3.1 Aqua-regia-extractable (total) metal concentrations

In all sediment samples, the highest element concentrations were generally found in the aqua-regia digests as compared with HCl and acid oxalate extracts (tables 1–6). The high Fe concentrations ($18\,275\text{--}23\,520 \mu\text{g g}^{-1}$) leached by aqua regia indicate that most of the iron exists as well crystalline oxides. This is consistent with the high abundance of magnetite (Fe_3O_4) and ilmenite (FeTiO_3) minerals in the River Nile sediments [26]. In the River Nile, iron oxides may result from the physical erosion of the drainage area already containing

Table 5. Total (aqua-regia-digestible) and extractable Cu and Pb concentrations ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

| Location | Cu | | | Pb | | |
|-----------|-------|-----------------|--------------------------|-------|-----------------|--------------------------|
| | Total | HCl-extractable | Acid-oxalate-extractable | Total | HCl-extractable | Acid-oxalate-extractable |
| Aswan 1 | 30.5 | 15.3 | 14.0 | 50.0 | 17.5 | 29.5 |
| Aswan 2 | 37.5 | 13.5 | 16.5 | 46.5 | 15.0 | 32.0 |
| Kom-Ombo | 37.5 | 12.8 | 23.0 | 60.0 | 18.0 | 39.0 |
| Edfu | 41.5 | 16.8 | 29.5 | 46.5 | 20.0 | 32.0 |
| Esna | 37.5 | 27.5 | 23.5 | 46.0 | 32.5 | 36.5 |
| Qena | 38.5 | 18.8 | 16.5 | 34.5 | 10.0 | 30.0 |
| Sohag | 36.0 | 23.3 | 20.0 | 38.5 | 20.3 | 28.5 |
| Assiut | 35.0 | 17.0 | 32.0 | 46.0 | 20.0 | 32.0 |
| El Menya | 33.0 | 22.0 | 21.0 | 44.5 | 25.0 | 33.5 |
| Beni Suef | 38.5 | 22.8 | 19.0 | 45.5 | 28.0 | 26.5 |
| Giza | 41.0 | 32.3 | 22.0 | 46.0 | 25.8 | 30.5 |
| Mean | 37.0 | 20.2 | 21.5 | 45.8 | 21.1 | 31.8 |

Table 6. Total (aqua-regia-digestible) and extractable Zn concentrations ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

| Location | Zn | | |
|-----------|-------|-----------------|--------------------------|
| | Total | HCl-extractable | Acid-oxalate-extractable |
| Aswan 1 | 121.5 | 90.0 | 115.0 |
| Aswan 2 | 109.5 | 30.0 | 36.5 |
| Kom Ombo | 123.5 | 30.0 | 75.0 |
| Edfu | 270.0 | 95.5 | 145.0 |
| Esna | 124.0 | 65.0 | 53.5 |
| Qena | 122.5 | 67.0 | 20.0 |
| Sohag | 149.5 | 49.5 | 17.5 |
| Assiut | 149.5 | 87.0 | 56.0 |
| El Menya | 132.5 | 70.0 | 57.0 |
| Beni Suef | 136.5 | 65.0 | 37.5 |
| Giza | 91.5 | 213.0 | 52.5 |
| Mean | 126 | 78.4 | 60.5 |

Note: Shaking time: 5 h; sediment: extraction ratio: 1:50.

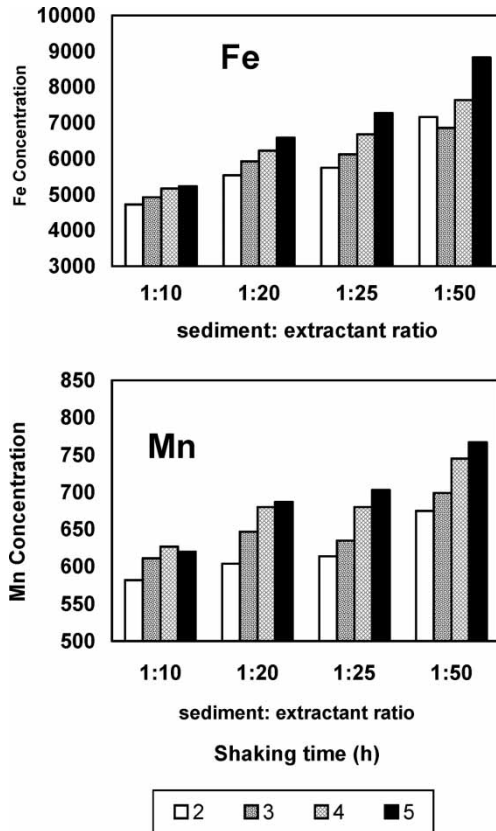


Figure 2. Mean HCl-extractable concentrations of Fe and Mn ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

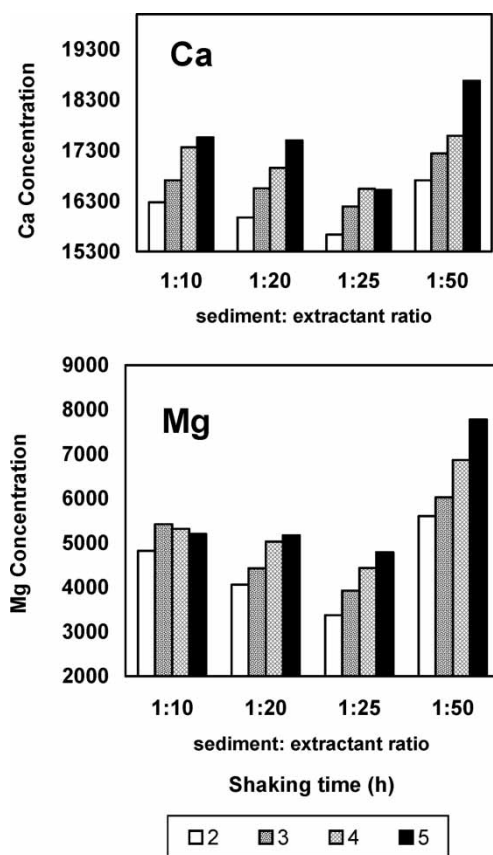


Figure 3. Mean HCl-extractable concentrations of Ca and Mg ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

iron oxides. Iron compounds were considerably concentrated in the fraction where bound to carbonate/metal oxide and bound to organic matter/silicate, and only 22% were found in the environmentally mobile fraction [27].

It is well known that the aqua-regia extraction technique provides a high degree of element extraction; it does not dissolve silicates completely but destroys organic matter, dissolves all precipitated and adsorbed metals, and leaches out a certain amount of metals from the silicate lattice [4, 28]. Furthermore, extraction with aqua regia (3:1 (v/v) HCl:HNO₃) has several advantages over other total element extraction techniques. Aqua-regia decomposition of sediment is sufficient for heavy-metal analysis for detection of pollution sources [29]. For these types of study, it is not necessary to obtain full digestion of all sediment compounds including resistant silicate minerals, since the pollution effects are usually associated with the surface sediment particles.

3.2 Acid-oxalate-extractable metal concentrations

Tables 1–6 show that considerable amounts of total element contents were extracted from sediment samples by acid oxalate reagent. These amounts represent the exchangeable and adsorbed forms and/or those bound to carbonate and organic matter as well as, but largely, those associated with amorphous oxides (freshly precipitated gel and aged amorphous oxides)

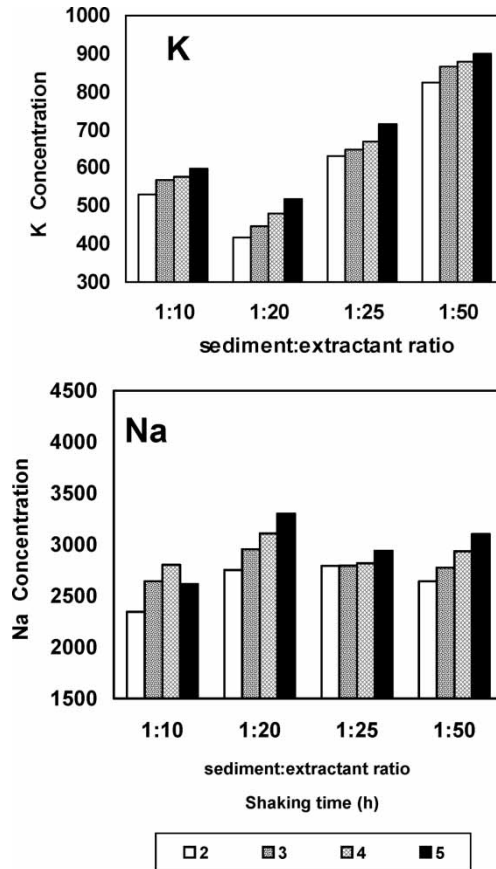


Figure 4. Mean HCl-extractable concentrations of K and Na ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

of iron and manganese [22, 30]. These element concentrations, in the course of changing the physicochemical properties of the water–sediment system, can be released into overlying water masses and equilibrate easily with solid phases.

Iron and manganese contents, on average, extracted by acid oxalate were 6370 and $513 \mu\text{g g}^{-1}$ and constituted 25.6 and 17.0% of the total concentrations, respectively. In contrast to Fe, the relatively low percentage of Mn extracted by acid oxalate solution agrees with the observation that in most natural waters of Mn(II), oxidation is a much slower process than Fe(II) oxidation [31]. For Mg, Na, and K, the observed concentrations represent an appreciable proportion of the total element concentrations: 36.5% Mg, 33.0% Na, and 24.1% K. The relatively high extractability of Mg by acid oxalate solution (pH = 3.3) reflects the ability of this reagent to dissolve the carbonate phases, to a certain extent. These findings suggest also that Na and K are possibly associated with sediments components as exchangeable and/or adsorbed ions.

The existence of Cd in undetectable concentrations in the acid oxalate extract can be explained by the formation of complexes between Cd and oxalate ions. These complexes may be adsorbed strongly onto the iron oxide and enhance the Cd readsorption; the enhancement is generally favoured at low pH.

In contrast to all the studied metals, a relatively low percentage of Co (11.3% of total content) was extracted by acid oxalate from the sediments samples. This is possibly attributed to the enrichment of Co in the residual phases. These results are in line with the known

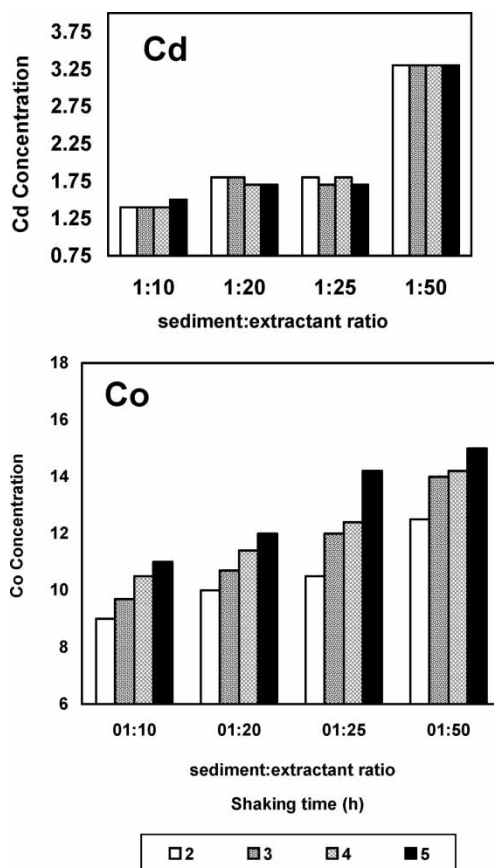


Figure 5. Mean HCl-extractable concentrations of Cd and Co ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

geochemical tendency of Co to be incorporated in the ferromanganese minerals [4]. The acid-oxalate-extractable Co concentrations seem to represent the exchangeable and adsorbed and/or those bound to carbonate as well as, but largely those associated with the amorphous Fe/Mn oxides. The importance of amorphous oxides, which are usually dissolved by acid oxalate, in regulating Co concentration in aquatic sediments has been demonstrated [32, 33]. Comparing the results, on average, it appears that very high percentages of the total concentration of Pb (69.4%), Cu (58.0%), and Zn (48.0%) were extracted by acid oxalate (tables 1–6). The high acid oxalate-extractable Pb concentration may indicate its association with Fe/Mn oxides or may be attributed to adsorption of Pb on potassium-rich minerals. This is consistent with the fact that Pb(II) can be incorporated into potassium-rich minerals by replacement of potassium with a similar ionic radius of about 1.3_ [34]. The low solubility of Pb in stream environment would appear to favour the formation of $\text{Pb}(\text{OH})_2$ particularly on increasing the pH of the solutions; sub-micron particles of such phases could be utilized as nucleation sites for Mn precipitation, and act as precipitants in coupled oxidation–reduction reactions leading to the deposition of manganiferous material [35]. In soils or sediments, the hydrous Fe and Mn oxides may hold significant proportions of some heavy-metal ions. These oxides are known to exist as separate phases, and there is evidence from electron microprobe analyses of surface soils that Pb and Co are concentrated in the Mn oxides, whereas Ni, Cu, and Zn are concentrated and distributed approximately equally between the Fe and Mn oxides [36].

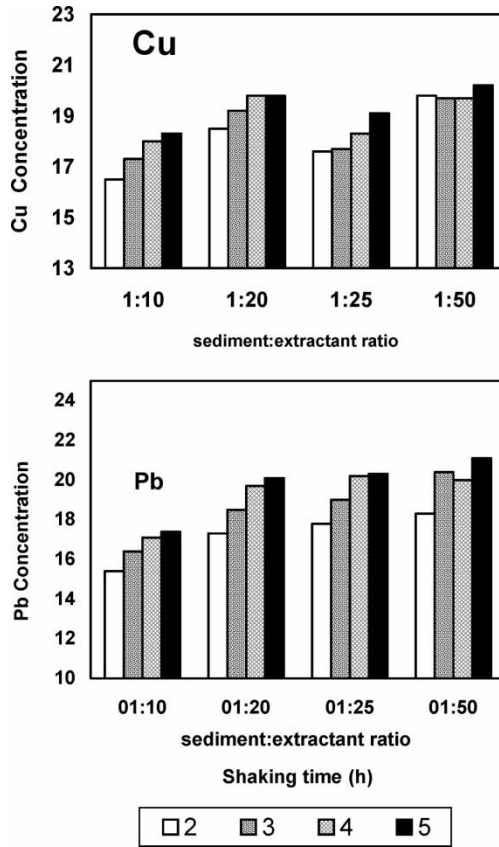


Figure 6. Mean HCl-extractable concentrations of Cu and Pb ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

The high percentage of the total zinc concentration extracted by acid oxalate solution may reflect the strong association with amorphous Fe/Mn oxides and/or may be attributed to its accommodation within clay minerals. These findings are in agreement with the known ability of amorphous Fe/Mn oxides to scavenge Zn from solution [19]. It has been shown that Zn

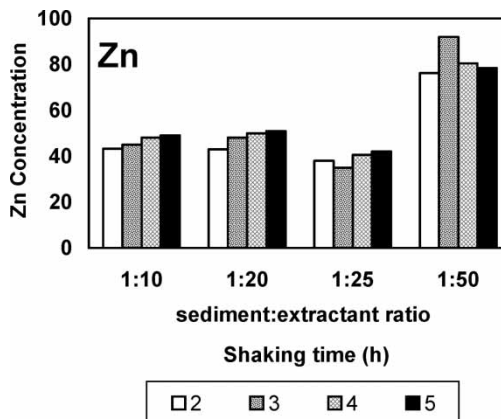


Figure 7. Mean HCl-extractable concentrations of Zn ($\mu\text{g g}^{-1}$ dry wt.) in the surface sediments of the River Nile from Aswan to Giza.

Table 7. Characteristics of the surface sediments of the River Nile from Aswan to Giza.

| Location | Carbonates (% as CaCO ₃) | Organic carbon (%) | EC ($\mu\text{S Cm}^{-1}$) | pH | Sediment fraction (%) | | | |
|-----------|---|-----------------------|---------------------------------|------|--------------------------|------------------------|---------------------------|-----------------------|
| | | | | | 63–15.6 μm | <15.6 μm | 15.6–3.9 μm | <3.9 μm |
| Aswan 1 | 9.1 | 0.75 | 1699 | 7.73 | 77.8 | 22.2 | 6.9 | 15.3 |
| Aswan 2 | 15 | 0.75 | 1681 | 7.6 | 43 | 57.04 | 32.3 | 24.7 |
| Kom-Ombo | 10.8 | 0.44 | 879 | 6.83 | – | – | – | – |
| Edfu | 14.2 | 1.8 | 464 | 7.39 | 44.3 | 55.7 | 29.9 | 25.8 |
| Esna | 10.6 | 3.48 | 560 | 7.08 | – | – | – | – |
| Qena | 12.5 | 0.99 | 856 | 8.26 | 64.6 | 35.4 | 17.7 | 17.7 |
| Sohag | 15.4 | 1.12 | 659 | 8.32 | 45.1 | 54.88 | 35.4 | 19.5 |
| Assiut | 8.8 | 0.46 | 735 | 8.25 | 69.5 | 30.5 | 12.8 | 17.7 |
| El Menya | 10.2 | 0.46 | 711 | 8.33 | 69.4 | 30.6 | 12.4 | 18.2 |
| Beni Suef | 12.3 | 0.72 | 801 | 8.3 | – | – | – | – |
| Giza | 14.4 | 0.99 | 1580 | 7.63 | – | – | – | – |
| Minimum | 8.8 | 0.44 | 464 | 6.83 | 43 | 22.2 | 6.9 | 15.3 |
| Maximum | 15.4 | 3.48 | 1699 | 8.33 | 69.5 | 57.04 | 35.4 | 25.8 |
| Mean | 12.1 | 1.96 | 1082 | 7.58 | 56.3 | 39.62 | 21.2 | 20.6 |

may be present in hydroxide-Al interlayers of 2:1 layer silicate and that Zn can be released during partial dissolution of the interlayer material by acid oxalate solution [37]. This is also supported by the high correlation coefficient value between Na and Zn ($r = 0.612$, $p < 0.01$) extracted by acid oxalate extractant.

3.3 0.5 M HCl-extractable metal concentrations

In the present work, the HCl extraction technique was studied in more detail to evaluate its suitability as an extractant for major and trace metals (including heavy metals) from River Nile sediments for pollution monitoring. The time required for dissolution of various associated metals depends on such factors as particle size and sample size (sediment:extractant ratio). To evaluate the optimum time for element extraction, sediment samples (<63 μm fraction) were subjected to single-step leaching procedures with 0.5 M HCl extractant for shaking times of 2, 3, 4, and 5 h at sediment:extractant ratios of 1:10, 1:20, 1:25, and 1:50.

Figures 2–7 show that both the contact time and the sediment:extractant ratio have a remarkable effect on the amount of metals extracted by 0.5 M HCl from sediment samples. It is clear that if reproducible and comparable results are to be obtained with the other extraction methods used, extraction conditions must be standardized. Therefore, preliminary experiments on the acid oxalate extraction method have been carried out using an extraction time of 5 h, and to prevent metal readsorption on active sites, which are possibly formed during the course extraction, leaching with 0.5 M solution was terminated after a maximum shaking time of 5 h.

Table 8 shows the values for extractability as a percentage of aqua-regia-extractable metal concentrations for the studied metals from the River Nile sediments by both HCl and acid oxalate extractants. In comparing the results, it appears that higher Fe and Mn concentrations were extracted by 0.5 M HCl than for acid oxalate. This indicates that 0.5 M HCl is able to dissolve not only the amorphous Fe/Mn oxides but also, to a certain extent, the more crystalline oxides of these two metals.

The amounts of Ca and Mg extracted by 0.5 M HCl solution were very similar to those extracted by aqua-regia reagent. This indicates that those two metals occur more extensively in easily acid-soluble forms (possibly as carbonate minerals) than in highly insoluble minerals. These results are also supported by the positive significant correlation between Ca and carbonate ($r = 0.556$, $p < 0.05$), Ca and Mg ($r = 0.739$, $p < 0.01$), and Ca and Zn

Table 8. Extractability as a percentage of aqua-regia-extractable metal concentration for the studied elements from the surface sediments of the River Nile by both HCl and acid oxalate extractions.

| Extractant | Element | | | | | | | | |
|----------------------|---------|------|------|------|------|------|------|------|------|
| | Fe | Mn | Mg | K | Na | Cd | Co | Cu | Pb |
| Zn | | | | | | | | | |
| 0.5 M HCl | 43.2 | 31.1 | 88.3 | 77.6 | 58.2 | 90.1 | 50.0 | 54.6 | 46.1 |
| 62.2 | | | | | | | | | |
| Acid oxalate, pH 3.3 | 25.6 | 17.1 | 36.5 | 24.1 | 33.0 | 22.1 | 11.3 | 58.0 | 69.4 |
| 48.2 | | | | | | | | | |

($r = 0.772$, $p < 0.686$, $p < 0.01$). Zinc ions show strong interactions with carbonate minerals ($\text{CaMg}(\text{CO}_3)_2$, MgCO_3 , CaCO_3 ; the finely dispersed carbonate particles act as accumulators for Zn ions [38].

The results also show very high percentages of total concentrations of K (77.6%) and Na (58.2%) extracted by HCl, suggesting that dilute HCl may attack some of the less resistant silicates, such as layer silicates. Comparing the obtained results, it is shown that the relative changes in the concentrations of Co and Mn extracted by 0.5 M HCl solution closely followed the relative changes in HCl-extractable Fe and Mg levels. This would suggest that these elements are, to a certain extent, associated with readily weathered ferromagnesian minerals. These findings are also supported by the good positive and significant correlation between Mg and Co ($r = 0.804$, $p < 0.01$) and Fe and Mn ($r = 0.427$, $p < 0.05$). Ferromagnesian minerals are distributed around the drainage area of River Nile [39].

For Co and Zn, the HCl-extractable concentrations were generally higher than the corresponding amounts extracted by acid oxalate. This is possibly attributable to the enrichment of Co and Zn in ferromagnesian minerals. Zinc and cobalt tend to follow Fe and Mn ions in ferromagnesian minerals. In contrast to all studied metals, higher concentrations of Pb and Cu were extracted by acid oxalate reagent. This could be ascribed to the tendency of these two elements to exist, to a certain extent, in organically complexed forms extracted by acid oxalate; the chelates of these two metals have high stability constants [40].

The fact that amounts of Fe, Mn, Ca, Mg, and Co extracted by HCl increase continually by increasing the time of extraction indicates that there are physicochemical forms of these metals released by 0.5 M HCl. On the other hand, the corresponding concentrations of Cd, Cu, and Zn were nearly constant for shaking times of 2–5 h, suggesting that these metals are present at the surface of oxides, carbonates, or organic materials, presumably as specifically adsorbed or chelated ions. In their study, Van Griethuysen *et al.* [41] found that the optimum time for Zn, Cu, Cd, Ni, and Pb extraction was similar to our observations (2–4 h) concerning metal-extraction efficiency. Also, Snape *et al.* [13] found that 1 M HCl acid extraction for 4 h is suitable as a standard method for assessing metal concentrations in sediments.

4. Conclusion

The present study has demonstrated characteristic effects of the sediment:extractant ratio and the length of the extraction period. Therefore, when a sediment analysis is used to identify and monitor pollution sources, this is imperative for base-metal analysis on a standardized procedure with regard to sample size, particle size, and shaking time. The extraction results obtained revealed that a sediment fraction <63 μm , sediment:extractant ratio of 1:50, and shaking time of 5 h are optimum conditions for leaching the bioavailable fractions of heavy metals from aquatic sediments.

Although the extraction data indicate that both 0.5 M HCl and acid oxalate reagents are able to extract both inorganic and organic association non-residual metals simultaneously, the 0.5 M HCl extraction technique is preferred. From an analytical chemistry point of view, unlike acid oxalate, HCl does not form sparingly soluble metal complexes. This is a reliable, rapid, harmless, simple, and inexpensive method for measuring bio-available or anthropogenic concentrations of metals in aquatic sediments. Unlike acid oxalate, the HCl extract is odourless and does not clog the atomizer of the spectrometer. Extraction with 0.5 M HCl obviates the need to use chemicals, some of which are toxic or unavailable readily as a high-purity grade. A standard extraction method should be relatively simple, in order to perform routine analyses of large numbers of sediment samples, yet at the same time it should provide sufficient information on the environmental impacts of particular metals. Therefore, dilute hydrochloric acid solution is very suitable for heavy-metal-pollution monitoring in the River Nile.

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